Ab initio simulations of H_2 in Li-doped carbon nanotube systems

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Because of their unique structure, it has been proposed that carbon nanotube ropes may well provide an ideal container for the storage of molecular hydrogen. Indeed, there has been some experimental evidence of enhanced hydrogen uptake in doped Li and other alkali metal systems [Chen *et al*, Science **285**, 91 (1999)]. We have therefore addressed this issue of hydrogen storage in Li-doped graphite and carbon nanotube systems theoretically with *ab initio* simulations. Our results find no evidence for such enhanced storage, based on the induced structural changes. In addition, we have also investigated the diffusion barriers for hydrogen to enter into nanotube interiors, both in the presence and absence of topological defects. Even if nanotube interiors are made accessible, the hydrogen uptake remains modest, *i.e.*, less than 3.5 wt%. Mechanically or chemically processing nanotubes is therefore not likely to lead to greatly increased hydrogen storage.

I. Introduction

It has long been recognized that molecular hydrogen is an almost ideal, environmentally friendly fuel [1]. However, to be truly useful, the technological ability to store hydrogen molecules must be considerably improved [2]. For these purposes, metal hydridization remains a distinct possibility, but is not a preferred solution because of the associated expense and weight. Carbon nanotubes ropes and other carbon-based systems have been proposed as alternative hydrogen storage materials. The key feature that makes nanotubes so potentially useful as a storage material is their structure. Carbon nanotubes [3] are formed when a graphene sheet is curled into a cylinder and the carbon atoms joined seamlessly to each other. During growth, individual nanotubes typically aggregate into bundles, termed *ropes*, which consist of potentially hundreds of nanotubes held together by van der Waals forces. These ropes are expected to display superior hydrogen uptake, provided that the hydrogen molecules can intercalate both into the channels between the nanotubes, and into the interior of the nanotube themselves. Based on these expectations, initial experiments of hydrogen storage in nanotubes were very encouraging: for instance, work by Dillon *et al* [4] reported an uptake of 7 weight (wt) percent of H_2 at 133 K and 0.04 MPa; Ye *and coworkers* [5] used high purity nanotubes and obtained 8.25 wt % at 80K and 7 Mpa. Unfortunately, subsequent experiments [6] failed to reproduce these results for a variety of reasons, so that the resulting controversy has not yet been fully resolved. More recently, another interesting

alternative for enhanced hydrogen storage was given by Chen and coworkers [7], whose experiments claimed to achieve up to 20 wt % uptake in Li-doped carbon nanotube systems, and up to 14 wt % for K-doped nanotube systems. These numbers are impressive and compare favorably with those of gasoline or diesel, which contain the equivalent of 17 wt %. This new approach has the additional advantage of operating at ambient pressures and modest temperature.

Motivated by these experiments, we have re-examined the question of hydrogen storage in carbon-based systems with *ab initio* simulations. In particular, we focus on the issue of enhanced hydrogen adsorption in Li-intercalated graphite and carbon nanotube systems. Unfortunately, in agreement with the most recent experimental results [8] and other simulations of hydrogen/nanotube systems, we find no evidence or mechanisms for enhanced hydrogen storage. In addition, since the key to enhanced hydrogen uptake in nanotube ropes is predicated on the ability of molecules to move in and out of the nanotube interiors, we have studied the diffusion barriers for hydrogen molecules to enter nanotube interiors. Both *pristine* and *defective* nanotubes have been considered. The latter is particular important, because defects may readily be induced in nanotube side-walls via mechanical [9] and chemical means [10] . Indeed, both experiments[11]and theory [13] show that Li-uptake in nanotube systems, for battery applications, is increased substantially when the nanotubes are first subjected to an intense ball-milling treatment. Our calculations show, that even when very large defects are present, there are substantial diffusion barriers present so that only moderate increases in the hydrogen uptake may be expected.

II. Results

(a) Methodology

To investigate the issue of hydrogen storage in Li-doped carbon-based systems, we performed *ab initio* density functional theory (DFT) based calculations using a real-space code with multigrid acceleration[17]. Nonlocal and norm-conserving pseudopotentials of the Troullier-Martins form[18] were employed using the standard Kleinman-Bylander form[19]. Calculations were carried out with a grid spacing corresponding to an effective cutoff of 63 Ry with 12 k-points. To calculate the diffusion barriers, we mapped out the point-by-point diffusion pathways, while keeping the orientation of the hydrogen molecules fixed. Calculations were carried out both with the local density approximation (LDA) and with generalized gradient corrections (GGA) of Perdew-Burke-Ernzerhof (PBE)[20]. For this issues related to hydrogen storage, both methods give very similar results, and hence we shall mostly quote only the LDA results, noting differences as they arise. We now turn to the results of our calculations. Since carbon nanotubes are structurally intimately related to graphene sheets, we first consider hydrogen molecules in graphite.

(b) H_2 in doped graphite

To investigate hydrogen adsorption in graphite systems, we first performed test calculations on pure graphite. In excellent agreement with previous calculations, we found the in-plane C-C bonds to have a length of 1.42 Å, while the c-axis – *i.e.,* the distance between the graphene sheets was found to be 3.35 Å, respectively. Next, we tested the energetics of adding a single H_2 molecule to the various symmetry sites. These different sites are shown in Fig. 1, while their energetics is summarized in Table I. For the pure graphitic system, the most favored site S_1 lies above a carbon atom, midway between two planar graphene sheets. Because of the ..ABAB.. stacking of the graphene sheets, other symmetry sites such as S_2, which is located inside an "empty" hexagonal site, S_3 and S_4, are somewhat less favorable, indicating that the hydrogen molecule is unlikely to insert into these positions.

Now consider hydrogen in Li-doped graphitic systems. Here, we focus on stage one intercalation with a Li uptake of one Li atom for every six carbon atoms, *i.e.,* LiC_6, since this configuration should lead to maximal hydrogen uptake. The presence of Li atoms is known to change the stacking of the graphene sheets from ..ABAB.. to ..AAAA.. In addition, Li transfers its valence electron completely to the graphene sheets. Figure 2 represents the structure of LiC_6, with the location of the different symmetry sites marked.

Table 1 summarizes the adsorption energies of H_2 at these sites. The minimum energy site in this case is located at S_1, which is located inside the "empty" hexagonal cells, midway between any two graphene layers. All other sites cost at least 0.2 eV more in energy. In all cases, the ideal configuration of the molecular hydrogen corresponds to the molecular axis being parallel to the graphene sheet as shown in Fig. 2 . As expected, the adsorption is a function of the molecular orientation, with other orientations of the hydrogen molecule being less favorable. For instance, for a hydrogen molecula at S_2 whose molecular axis is perpendicular to the graphene sheet is 0.22 eV less favorable. Similarly, an orientation with the molecular axis around 45^0 is less favorable by about 0.5 eV.

Having identified the ideal adsorption sites, we turn to the thermodynamics of hydrogen uptake. At low temperatures, the chemical potential μ is well approximated by $\mu = E_{System+H_2} - E_{System} - E_{H_2}$, where quantities like $E_{system+H2}$ represent the total energy of the system with an adsorbed hydrogen molecule. For a graphite system, we obtain $\mu = 2.3$ eV, in agreement with previous investigations[21]. For Li-intercalated graphite, we obtain $\mu = 0.144$ eV for hydrogen adsorption at the most favorable sites. Clearly, since these values are positive, hydrogen uptake is not thermodynamically favored for either of the two material systems. What is the origin of the large change in the chemical potential? It is largely due to the change in the ABAB to AAAA stacking, and a swelling of the Li-intercalated compound. For instance for Li-intercalated graphite, the addition of a single hydrogen molecule per unit cell causes a dramatic swelling of the distance between the graphene sheets, we note at least a substantial 24

percent change. To provide further evidence of this effect, we have studied the change in chemical potential as a function of distance between the graphene sheets. We find that a very large distance of 4.6 Å is required before μ becomes nearly zero (Fig. 3). Such a large change implies that it very unlikely that there is any significant hydrogen uptake in either of these two graphite-based systems.

(c) H_2 in doped carbon nanotube ropes

Having discussed hydrogen adsorption in Li-doped graphite, we turn to adsorption in Li-doped nanotube systems. Nanotube ropes consist of bundles of nanotubes whose centers are arranged in a hexagonal pattern. *Li* ions intercalate into the ropes primarily in the channels between the nanotubes with a *1:6* ratio. Associated with the Li intercalation is a slight swelling of carbon nanotube ropes, which changes the distance between the nanotubes from 3.3 to 3.42 Å. Now, in its *local* structure, carbon nanotubes are very similar to planar graphite sheets, so that in terms of hydrogen adsorption we can expect very similar results. To test this we constructed a prototypical nanotube rope out of (5,5) armchair nanotubes. Inside this rope, we placed 6 Li atoms per unit cell; each unit cell contained 40 carbon atoms. Hydrogen molecules were then added to the system as in the case of Li-intercalated graphite and the chemical potential changes were computed as already described. The results are similar to those obtained for the graphite system: only by greatly increasing the distance between nanotubes does it become thermodynamically favorable for hydrogen molecules to adsorb into the system. Hence, similar to the case of hydrogen adsorption into the interstitial channels of nanotube ropes, we do not expect significant amounts of hydrogen molecules to be stored in the corresponding Li-intercalated system. For instance, in our estimate, we could put at most 2 H_2 molecules for a (10,10) nanotube at the interstices.

What about hydrogen molecules entering nanotube interiors? Clearly, hydrogen molecules must be able to diffuse into and out of these interior regions at a reasonable rate if carbon nanotube systems are to act as a convenient molecular container. To probe the ability of hydrogen molecules to enter a nanotube interior, we calculated the energetics of a diffusion pathway for the molecule to move through the sidewall of a (5,5) nanotube. While there are diffusion minima on either side of the nanotube wall, a very large barrier of about 10.72 eV is encountered, so that it is very unlikely that hydrogen molecules can diffuse into nanotubes through pristine sidewalls. Hence, other pathways into the nanotubes must be found. A possible option here is provided by the various topological defects that can be induced in the nanotube walls by such nonequilibrium means such as ion bombardment [10], tensile straining, or by the mechanical grinding of nanotubes [22, 23]. The spirit here is similar to previous work on Li-intercalation into nanotube systems. While initial experimental results showed a relatively poor 25% increase of Li

uptake relative to graphite, better results were achieved by first ball-milling [11] the carbon nanotube samples. This not only dramatically reduced the irreversible Li capacity of nanotubes, but also increased the reversible capacity to about 2.7 Li atoms per 6 C atoms.

One can expect that the structure of nanotube defects to vary considerably, depending on how they are induced. However, the relevant feature of all the various defects is that they consist of n-membered rings in various combinations. Hence, we focused on the diffusion barriers for hydrogen molecules such rings, as shown in Fig. 5. Note that once formed, we can expect these metastable structures to persist for very long periods of time because of the high activation energies required for bond rotations[12]. Table II summarizes the diffusion barriers for hydrogen molecules to enter nanotube interiors.

As expected, as the number of sides increases and the "holes" become larger and larger, the diffusion barriers drop. However, even for 10-sided rings or decagons, a significant barrier of 1.6 eV in encountered. Hence, defects larger than decagons are required for efficient hydrogen motion in and out of nanotubes interiors. These results are quite different from the case of Li ions, for which the diffusion barriers are all about 1-2 eV lower indicating that enhanced Li uptake through defects is indeed possible[13].

Finally, the only other way in which hydrogen molecules can enter nanotube interiors is via their open ends, provided that such tubes can be stabilized. To be useful, such open-ended tubes would have to be relatively short in order to allow for a reasonable rate of molecular exchange. To place a hydrogen molecule inside an open nanotube, we find that there is essentially no diffusion barrier. In fact, there is a small net decrease in the chemical potential of the system of about 0.16 eV, indicating that a single hydrogen molecule is readily pulled into the nanotube interior. Similarly, a second hydrogen molecule may be added to a unit cell consisting of 4 rings of a (5,5) nanotube (40 atoms) at virtually no cost in in terms of a chemical potential. However, we find that adding a third molecule requires a $\mu = 1.09$ eV. Hence, a (5,5) nanotube interior will only hold 2 hydrogen molecules for every 4 rings giving a relatively small ratio of 0.76 weight percent. Since larger diameter nanotubes should in principle be able to accommodate more hydrogen molecules, based on geometry, we performed both LDA and GGA calculations for an Li doped (10,10) nanotube (*1:6* ratio) in order to assess the size (diameter) dependence of the nanotubes on the hydrogen to carbon ratio. We obtained 3.33 wt % and 2.24 wt % (the wt % from the interstitial sites was included) for hydrogen intake using LDA and GGA respectively. In the LDA calculation, the nanotube interior held 16 hydrogen molecules per 80 carbon atoms arranged in two heptagonal layers, whereas for GGA the configuration was pentagonal; finally, in the LDA case only, among the 16 molecules, 2 hydrogen molecules were located along the nanototube axis as shown in

Fig. 4. While there is a net increase compared to a (5,5) tube, the hydrogen to carbon ratio is not boosted sufficiently. Thus, even if nanotube interiors are somehow made accessible, one can still only expect relatively small uptake of hydrogen molecules.

III. Summary

We have investigated the uptake of hydrogen molecules in Li-doped graphite and carbon nanotube systems with *ab initio* simulations. For both systems, there is no evidence that doping with alkali metals should lead to significant increases in the adsorption of molecular hydrogen[14, 27]. Molecular hydrogen does not readily intercalate into pure a graphite, unless the distance between the graphene sheets is artifically enlarged. Similar results hold for the Li-doped graphite and carbon nanotube ropes, although the chemical potential needed to add a hydrogen molecule is significantly reduced. Our theoretical results are therefore not consistent with the original experiment of Chen et al[?]. We speculate that a suitable explanation for this discrepancy has been recently found by Pinkerton and coworkers[24], who attribute the enhanced hydrogen uptake in the original experiment to water contamination. In addition, we have studied the diffusion barriers for hydrogen molecules to enter into nanotube interiors. Because of the very large diffusion barriers, molecular hydrogen cannot enter through nanotube sidewalls. Preprocessing nanotube samples by mechanical means such as grinding will require the introduction of large-ring topological defects (greater than decagons) in order to enable access to nanotube interiors. However, even if nanotubes interiors are accessible, the hydrogen uptake is still modest.

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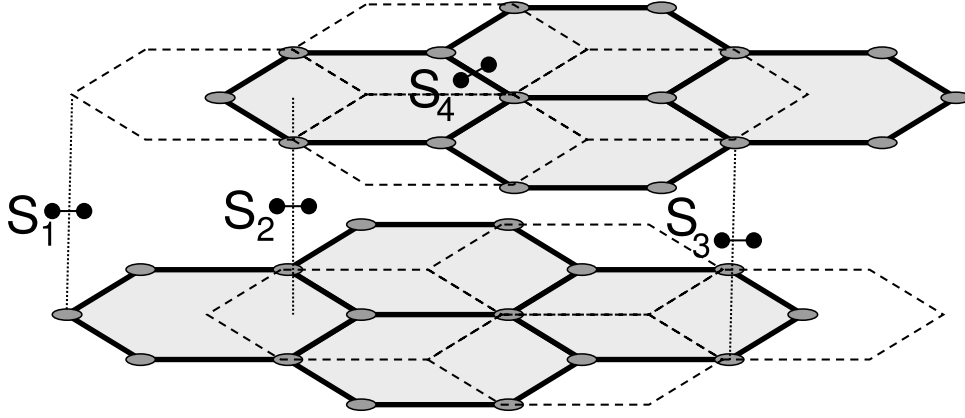[27] G. E. Froudakis, J. Phys. Condens. Matter **14**, R453-R465 (2002).

FIG. 1: H_2 molecule at the symmetry sites (..AB.. stacking). S_1:H_2 molecule is over the carbon atom. S_2:H_2 molecule is inside an empty hexagonal site. S_3:H_2 molecule is between two carbon atoms. S_4:H_2 molecule is over the bridge. In all these configurations the H_2 molecule axis is held parallel to the layer.

TABLE I: Energies (eV) for H_2 absorption sites, measured with respect to the value at S_1.

	S_1	S_2	S_3	S_4
Carbon	0	0.19	0.38	0.76
Carbon-Li	0	0.22	0.46	0.65

TABLE II: Diffusion barriers for hydrogen to move through a given n-membered ring.

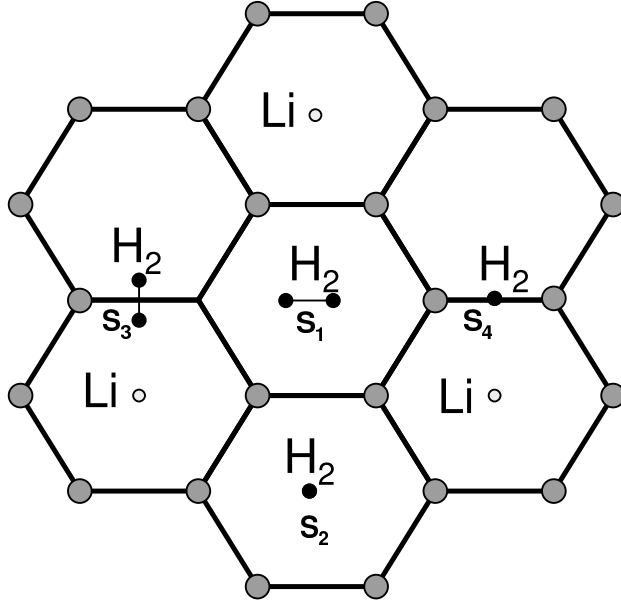| N-sided rings	Hexagon	Heptagon	Octagon	Enneagon	Decagon
ΔE (eV)	10.72	7.75	5.68	2.23	1.63
Formation (eV)	0.0	3.5	6.2	9.5	-

FIG. 2: Energetically favorable configurations for H_2 molecule approach to the graphene layer in Li doped graphite (..AA.. stacking, for view). S_1: H_2 molecule, at the center of hexagon, parallel to layer. S_2: H_2 molecule, at the center of hexagon, orthogonal to layer. S_3: H_2 molecule, over C-C bond, parallel to layer. S_4: H_2 molecule, over C-C bond, orthogonal to layer.
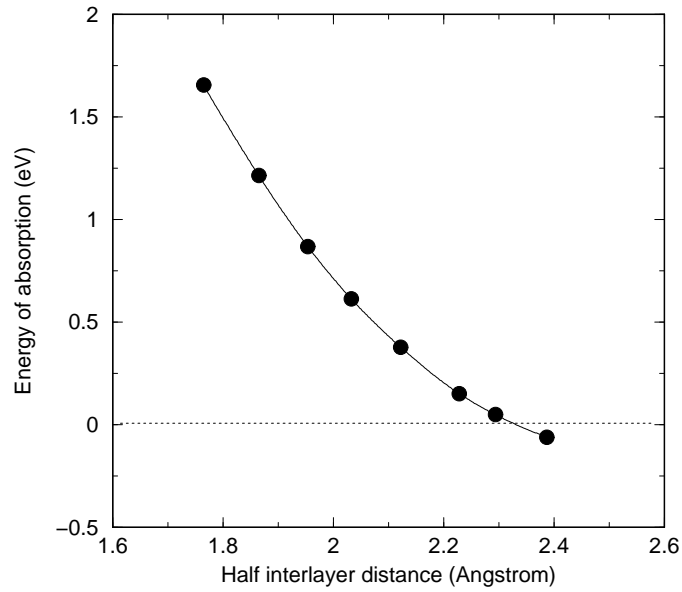

FIG. 3: Energy of absorption for LiC_6H_2 unit cell (..AA.. stacking). The curve is not a fit, but simply a guide to the eye.
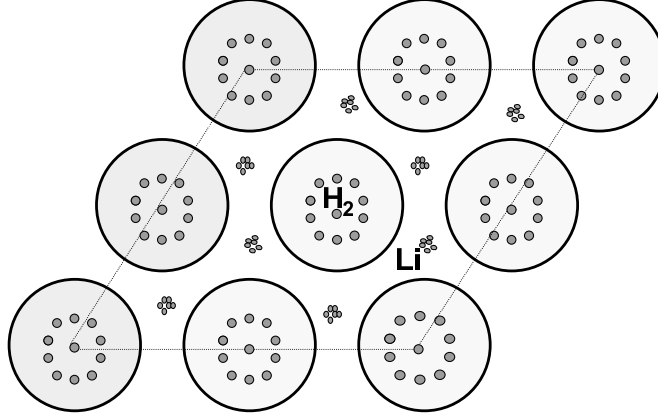
FIG. 4: Top projected view of hydrogen and lithium intercalation in nanotube ropes. Lithium atoms (not coplanar) are in the interstitial channels while H_2 molecules are in the nanotube interiors.
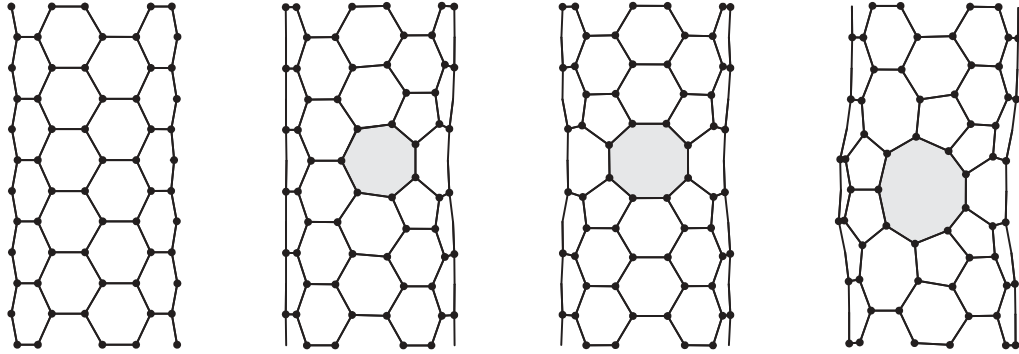

FIG. 5: Structure of the topological defects displaying different n-membered rings. The diffusion barriers through these rings and the corresponding formation energies are given in Table II.